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1 SECTION 1

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2 GROUNDWATER TRACER TEST AT WAIKAKALAUA FUEL

3 STORAGE ANNEX

4 A groundwater tracer test was conducted at Waikakalaua Fuel Storage Annex (FSA) between July 27, 5 2001 and October 28, 2001 to provide information to assist in evaluating the transport of dissolved 6 petroleum compounds in the Pearl Harbor basal aquifer observed at monitoring well ST12MW03. The 7 test consisted of injecting a mixture of fluorescein dye and potable water into the aquifer at ST01MW03 8 over a six-day period, and periodically collecting groundwater samples for analysis at ST12MW03, 9 ST12M009, and RW001 over the following two months. The test was conducted in response to 10 groundwater sample results collected at ST12MW009, which indicated that no petroleum compounds 11 were detected. At that time, estimates of the groundwater gradient at Waikakalaua FSA were based on 12 groundwater potentiometric surface measurements, and indicated that ST12MW009 was located approximately 108 feet on a bearing of 139 degrees southeast, directly hydraulically downgradient from 13 14 ST12MW03. In addition, ST12MW009 is located between the known groundwater petroleum plume and 15 the nearest drinking water well 2600-002 (Dairy Co. Well). RW001 is located approximately along the 16 flow vector indicated by the regional groundwater model at a distance of approximately 525 feet on a 17 bearing of 175 degrees south-southeast from ST12MW03. Following the results of the tracer test, the site 18 monitoring wells were resurveyed in October of 2002. Errors in the original elevation measurements 19 were discovered and corrected. At this time, the groundwater gradient was recalculated from historic 20 water level measurements. Based on these calculations, the gradient vector has ranged between 190 and 21 234 degrees south-southwest. It was hoped that the tracer test would provide important information about 22 transport times and rates of natural attenuation. Although the results did not clearly provide travel times 23 and attenuation rates, they did provide data which indicates that retardation is potentially a much bigger 24 factor in particle transport than previously anticipated.

1.1 PRELIMINARY MODELING AND COMPUTATIONS

26 Based on the best groundwater flow direction estimates available at the time, ST12MW009 was installed 27 directly down gradient from the Open Bottom Disposal Basin (OBDB) at ST12C, placing this well approximately 100 feet (ft) to the east of a direct down-gradient flow line from ST12MW03. However, 28 29 the accuracy of the calculated flow direction was questionable. The water table is very flat (the average 30 maximum difference in water level is approximately 0.3 feet across the site); therefore, small errors in survey elevation, Total Vertical Depth (TVD) correction, or depth to water measurements could result in 31 32 a significant error in calculated flow direction. To better design the tracer test and increase the chance of tracer detection at ST12MW009, various tracer injection scenarios were tested by running the Modular 33 34 Three-Dimensional Flow Model, Modular Three Dimensions (MODFLOW/MT3D) models. 35 MODFLOW is a widely used United States Geological Survey (USGS) groundwater model that simulates 36 groundwater flow in three dimensions (Macdonald and Harbaugh, 1988). MT3DMS (Modular Three 37 Dimensions Multi-Species Transport Model) utilizes the groundwater flow solution from MODFLOW to 38 simulate the transport of dissolved constituents (Zheng and Wang, 1999).

39 The hydraulic head was fixed for the model boundary upgradient from ST12MW03. Likewise, the

40 hydraulic head for the model boundary downgradient from ST12MW009 was also assigned. These

41 values were based on the most recent hydraulic gradient and flow direction calculations that were

- available when the tracer test was conducted. The values for hydraulic conductivity and porosity used in
- 2 the model runs were 1,500 feet per day (ft/d) and 0.10, respectively, which are representative values for
- 3 flank lava aquifers. A dispersion coefficient of 5 ft was assigned to account for hydrodynamic dispersion
- 4 as the tracer was transported from the injection point. In the simulation, tracer at a concentration of 60
- 5 parts per million (ppm) was injected at 1.5 gallons per minute (gpm) for six days. The model predicted
- 6 that the maximum dye concentration of 55 parts per billion (ppb) would pass through ST12MW009
- 7 approximately 46 days after injection began, as shown in Figure 1. More importantly, the model showed
- 8 that a short, highly concentrated pulse injection of dye would not result in detection of the dye at
- 9 ST12MW009, whereas a prolonged injection of dye would generate a large enough plume to be easily
- detectable at ST12MW009.
- 11 Fluorescein was selected as the tracer dye because it is non-toxic, will not sorb onto the solid matrix in the
- aguifer, and is detectable at low concentrations, with a detection limit of approximately 1 ppb in clean
- water. Using the manufacturer specifications for fluorescein and the criteria developed by Garth et al.,
- 14 2001, density calculations were conducted to ensure the density gradient created would not result in
- density driven flow and cause the bulk of tracer to pass beneath the well screen. Calculations showed that
- 16 a tracer concentration of 100 ppm or less would not result in any significant density driven downward
- 17 migration of the tracer.

1.2 EXPERIMENTAL DESIGN

- 19 The experimental plan called for injecting approximately 12,000 gallons of diluted tracer over a period of
- 20 nearly six days. A significant amount of pure water was required to conduct the tracer test. To deliver
- 21 the water, a three-fourth inch (in) diameter plastic water hose was connected between the Wheeler Army
- Airfield water main, just below the gate, to the inside of the compound, and ST12MW03. A constant flow
- device, designed to deliver 1.5 gpm, was placed in series with the hose near ST12MW03, followed by a
- 24 constant flow device and an activated charcoal filter with a purification capacity of 9,000 gallons. Prior
- 25 to connecting the supply hose to the rest of the injection system, a constant flow of 1.5 gpm was verified
- 26 by measuring the amount of time required to fill a four-gallon bucket. The schematic for this
- instrumentation is provided in Figure 2.
- 28 The dye needed to be added to the injectate was determined in a precise and predictable rate. The
- 29 concentrated fluorescein was diluted by a factor of adding two gallons of water for every gallon of
- 30 concentrate. The tracer solution was then poured into a five-gallon storage tank. A metering pump was
- installed on top of a tank and set to deliver the dilute solution to the injection system at a rate of 0.10
- 32 gallons per hour (gph). After calibrating the metering pump settings, the discharge of the metering pump
- 33 was connected to the water delivery system. To mix the dye with the dilution water, a tortuous path made
- 34 up of a series of 90 degree polyvinyl chloride (PVC) elbow joints, connected by short lengths of one-inch
- 35 PVC, was installed just past the dye injection point. A wye connection was placed in the injection
- 36 manifold past the mixing manifold. The injection hose was connected to one port of the wye and the
- other port was used to sample the injectate to verify the dye concentration during injection. Enough
- injection hose was connected so the discharge of tracer occurred beneath the water table.
- 39 To initiate injection, the supply valve on the water main was opened, while both valves on the wve
- 40 remained closed. The sampling port of the wye was then opened and a steady flow of 1.5 gpm was
- 41 verified. Next, the metering pump was started and the discharge from the sampling port was observed.

- When the color of water from the discharge port was uniform, indicating proper mixing of the dye, the
- 2 injection port was opened and the sampling port was closed.

3 1.3 TRACER SAMPLING

- 4 The tracer injectate was sampled during injection at the well head of ST12MW003. During injection,
- 5 sampling was conducted to test the accuracy and precision of the mixing apparatus. After injection was
- 6 terminated, samples were collected at ST12MW03, ST12MW009, and RW001. ST12MW03, the
- 7 injection well, was sampled during the monitoring phase to monitor the transport of the tracer from the
- 8 injection area, and ST12MW009 and RW001 were sampled during the monitoring phase to monitor the
- 9 down gradient transport of the tracer.
- 10 The day after the tracer injection was started, a sample was taken by opening the sampling port and
- closing the injection port. The sample container was filled, the tracer injection was resumed as before.
- 12 Injectate samples were taken daily until the injection was terminated. Approximately 5.5 days after the
- injection began, a final injectate sample was taken and injection was terminated. The injection hose was
- then withdrawn from the well. A sample was taken from the well by lowering two 1.5-inch by 36-inch
- 15 PVC disposable bailers into the well. The bailers were attached to a six-foot stainless steel rod so one
- bailer could retrieve a sample from the upper part of the well bore and the other bailer could retrieve a
- sample from the lower part of the well-bore. The samples were decanted into opaque, brown one-liter
- 18 sample bottles and submitted to Aecos Laboratories. Similarly, a sample was retrieved from
- 19 ST12MW009, except only a single bailer was used.
- 20 Samples were analyzed using a Turner AU-10 Fluorimeter. The Fluorimeter displays concentration in
- 21 Fluorescent Units (FU). To convert FU to ppm of fluorescein, a series of calibration samples were made
- 22 by diluting the concentrated fluorescein solution with distilled water. Calibration samples with a
- concentration of 75 ppm, 7.5 ppm, 0.75 ppm, 0.075 ppm were mixed and submitted to the laboratory for
- 24 analysis. A linear regression was done to develop a function for converting FU to a concentration of
- 25 fluorescein. To allow field analysis of the tracer samples, those calibration samples with visible
- 26 concentrations (those 0.75 ppm and greater) of fluorescein were analyzed in a Hach DR-820 Colorimeter.
- 27 Similarly, a function was developed to convert turbidity units to fluorescein concentration.
- After injection termination, samples were collected from ST12MW03 and ST12MW009 once every three
- 29 to four days for approximately 45 days. After 45 days, the sampling interval was increased to seven days
- 30 for the next two months. RW001 was added to the sampling schedule one month after injection was
- terminated. The bailer sampling was terminated in early January 2002 because the nearly constant tracer
- 32 concentration at ST12MW03 and lack of tracer detection at any other well indicated that sampling could
- 33 be done less frequently. Subsequently, samples were collected in conjunction with the semi-annual
- 34 Hickam POL long-term monitoring sampling. This sampling continues, with samples taken after
- 35 December 2001 being analyzed by the University of Hawaii, Water Resources Research Center (UH-
- 36 WRRC).

37

1.4 RESULTS

- The initial samples collected from ST12MW009 appeared to have fluorescence that exceeded background
- 39 values. This was also true for some samples collected at RW001. The samples were filtered and re-
- 40 analyzed twice at the Water Resources Research Center at the University of Hawaii and no detection of

- 1 tracer in any sample, other than in those samples collected from the injection well, could be confirmed.
- 2 Techniques are being developed at the UH-WRRC to concentrate the dye in water samples so that the
- 3 detection limit is in the fraction of the ppb range.
- 4 The tracer test model predicted that the dye concentration at the injection well would decrease to below
- 5 visually detectable concentrations approximately 25 days after injection was terminated. Furthermore, the
- 6 model predicted that the dye concentration would decrease below the analytical detection limit of 1 ppb
- 7 approximately 60 days after injection was terminated. Figure 3 compares the modeled and the measured
- 8 concentrations of dye at the injection point for the period from the termination of injection to 60 days
- 9 after injection was terminated. At 60 days after injection was terminated, the modeled tracer concentration
- at ST12MW03 was below detectable concentrations, while actual tracer concentration was still easily
- visible at 1 ppm. The cause of the persistence of the tracer is not known. The early rapid decrease in dye
- concentration implies the cause could be advection (the movement of dissolved constituent with flow of
- groundwater) transported dye from the injection area, as the model predicted. The modeled and analytical
- results were fairly close for the first week following injection. However, after the first week, the modeled
- and actual concentrations began to diverge, with the decay in the actual dye concentration slowing
- significantly when compared to the modeled decay.
- 17 Figure 4 shows the decay of the dye concentration from the time injection terminated until March of 2003
- 18 (the September 2003 sample has not yet been analyzed). The dye concentration has decreased from 36
- 19 ppm at the time the injection was terminated to 0.2 ppm in a sample taken on April 9, 2003. The dye
- 20 continues to persist at visually detectable concentrations as recently as September 2003, more than two
- 21 years after injection was terminated.

22 1.5 DISCUSSION AND CONCLUSIONS

- 23 It is assumed that that there is no significant interaction between dissolved constituents and the fractured
- 24 rock matrix that would retard the movement of dissolved constituents such as the tracer or dissolved
- 25 contamination. Therefore, the groundwater velocity should have been high enough to purge the injection
- well of tracer within two months after injection was terminated.
- 27 However, this experiment produced two unexpected results. First, there was no confirmed detection of
- tracer at either down gradient well. Second, the tracer persisted at visible concentrations at the injection
- well far longer than the prevailing assumptions predicted.
- 30 A review of the original survey data for WFSA revealed that the assumed top of casing elevations for the
- wells installed prior to 1997 were incorrect. This shifted the best estimated ground water flow direction
- 32 approximately 70 degrees to the west, placing ST12MW009 and RW001 well outside of the dye plume
- 33 migration from ST12MW03. However, due to uncertainty in the actual groundwater flow direction, these
- 34 wells will continue to be sampled for the Hickam POL long-term groundwater monitoring investigation,
- as well as to determine whether dye is present in these samples.
- 36 Although the dye was not detected at ST12MW009 or RW001, the persistence of tracer at ST12MW03
- may be significant. Like the tracer, low level contamination at ST12MW03, has been consistently
- detected each sampling round at fairly constant concentrations, but there have been no repeated detections
- 39 of WFSA related contaminants in any of the others wells. It is assumed that there is very little or no
- 40 sorption associated with transport of contaminants through fractured basalt. Furthermore, the
- 41 groundwater recharge at the site has been very low for the last several years due to lower than normal

- 1 rainfall on Oahu. This minimizes the addition of contamination from the vadose zone. The persistence of
- 2 the contamination at ST12MW03, with little addition of new contamination from the vadoze zone,
- 3 implies that, like the tracer, the contamination is less mobile than originally predicted by the prevailing
- 4 transport assumptions. These assumptions being that there is very little interaction between the dissolved
- 5 constituents in the groundwater and the surrounding rock matrix, and that the dissolved components are
- 6 transported by advection and hydrodynamic dispersion provide the only mechanism to increase the size of
- 7 the plume.

- 8 Application of the previously stated assumptions predicted that the relationship between time and tracer
- 9 concentration as a tracer passes a given point would form a uniform bell shaped curve. In actual field
- tracer test studies conducted in fractured rock, the slope of the trailing edge on the curve is much less
- steep, giving the bell a prolonged "tail". The leading hypotheses for the prolonged trailing edge on a
- tracer test in fractured rock media are listed below.
 - There are many advective transport paths in a fractured media. The individual hydraulic conductivity of each of these paths differs by orders of magnitude, with some fraction of the tracer being constrained to the low hydraulic conductivity paths. The arrival time of the tracer in the low hydraulic conductivity paths is delayed compared to the majority of the tracer that flows in the high hydraulic conductivity conduits (Becker and Shapio, 2000).
 - When tracer is injected into a fracture matrix, some of that tracer diffuses into the fractures. Diffusion is a kinetic process taking time to occur, and the time is dependent on the concentration gradient in the water, the diffusion coefficient of the tracer in water, and density of fractures in the media. The advective transport processes bypass the tracer fraction that diffuses into the fractures until the tracer concentration in the flow paths decreases below the tracer concentration in the fractures. At this time, direction of the diffusions reverses and the tracer starts to diffuse out of the fractures into the advective transport channels. This back diffusion is a slow process, but works to keep the tracer concentration elevated above what it would be in a pure advective process (Maloszewski and Zuber, 1993).
 - The third process is similar to diffusion into fracture, but it also states that some fraction of the tracer is diffused into solid matrix. Experiments have demonstrated diffusion of tracer into chalk and granite (Birgersson and Neretnieks, 1990). The diffusion into, and back diffusion out of, a solid matrix is a much slower process than diffusion into and out of fractures, and would work to further prolong trailing edge of time versus tracer concentration plot.
 - The reason the dye persists at ST12MW03 is unknown. A cause related to the procedures used during the tracer test cannot be discounted. However, experimental error or well design becomes a less logical choice the longer the dye persists and as more water is removed during the routine sampling process, it is more logical to assume that there is some process in the aquifer that retards the movement of tracer. The large amount of dye solution injected and the prolonged period of injection should have provided sufficient time for diffusion into fractures and possibly into the solid matrix. If diffusion into non-transport regions of the aquifer media can be confirmed, this would identify a retardation process that has not been accounted for in the contamination migration assessments. Furthermore, this would mean that dissolved contamination is much less mobile in fractured media than currently thought.
- Work is continuing at UH-WRRC to attempt to interpret the results of this experiment and the implications of delayed contaminant transport on risk assessments for this and similar sites.

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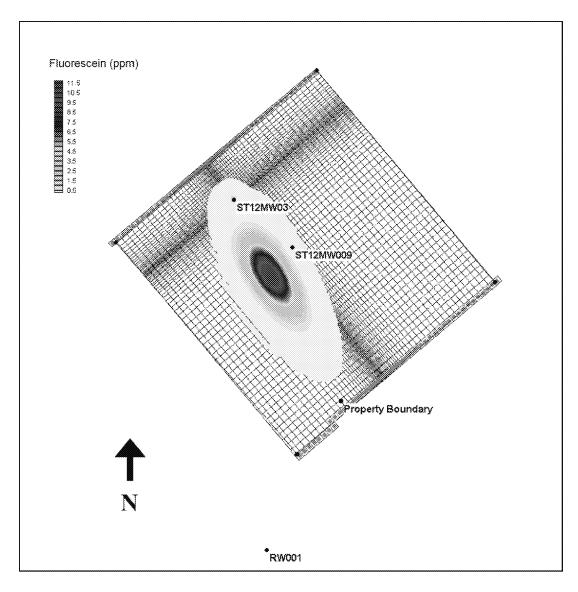


Figure 1. Modeled Tracer Plume 40 Days After Injection Was Terminated

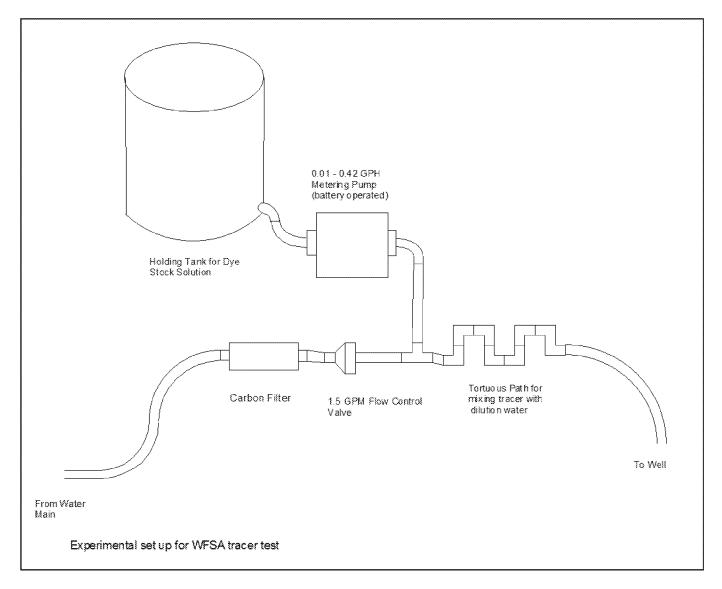


Figure 2. Schematic of Injection Instrumentation

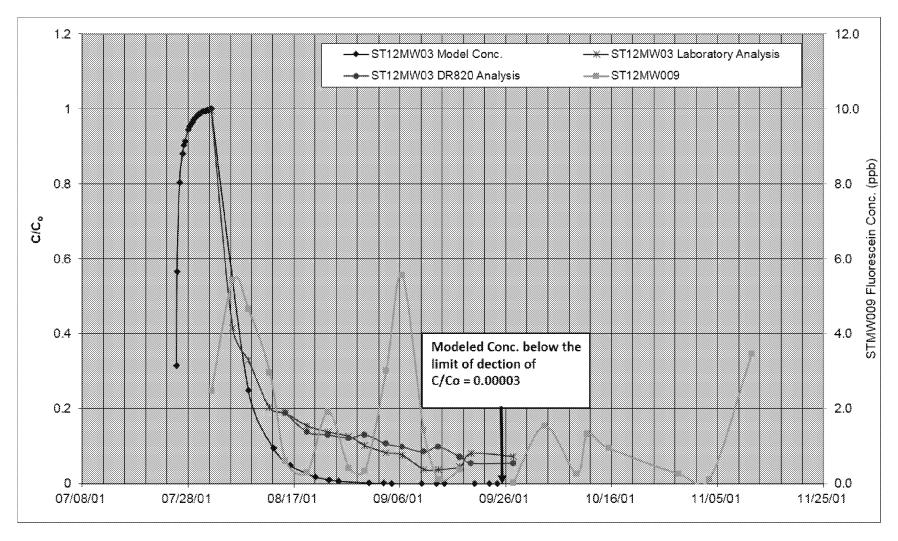


Figure 3. A Comparison of Actual and Modeled Tracer Concentration, 100 Days Following Termination of Tracer Injection

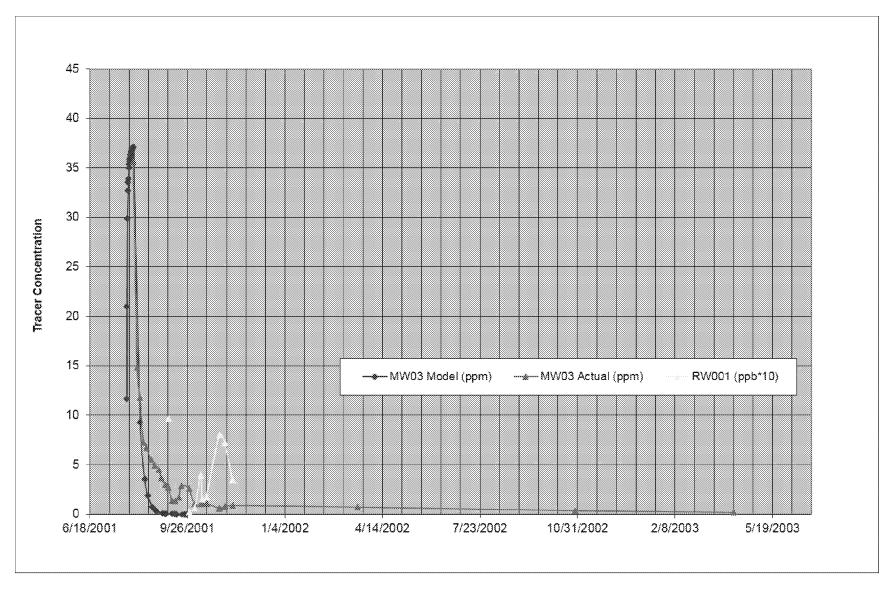


Figure 4. The Decay of Tracer at ST12MW03 From the Termination of Injection Until April 2003

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